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The effect of alkali metals doping on properties of $Cu/ZnO/Al_2O_3$ catalyst for water gas shift

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ABSTRACT

The following contribution shows the results of investigations on an influence of alkali metals compounds on physicochemical and catalytic properties as well as the most important operating parameters of Cu/ZnO/Al2O3 system, with a composition being similar to typical industrial heterogeneous catalysts for LT-WGS process. The addition of cesium or potassium to the Cu/ZnO/Al2O3 catalyst causes a decrease of copper surface. It gives remarkable inhibition of methanol synthesis, accompanying by a relatively small influence on the activity towards WGS.

Water–gas shift (WGS) is an important process carried out in hydrogen and syngas manufacturers, especially in the case of installations based on steam reforming of hydrocarbons (SR). Steam reforming of hydrocarbons followed by WGS is a dominant method of synthesis gases production, which are essential for most of important chemical processes e.g. ammonia production.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H_{298\,K} = 205.9\,kJ/mol \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H_{298\,K} = -41\,kJ/mol \tag{2}$$

In order to achieve the maximum efficiency of H_2 production, the water–gas shift process is conducted in two stages. The high temperature stage (HT-WGS) is performed at 340–450 °C in the presence of Fe–Cr–Cu catalysts. The low temperature stage that enables more thorough conversion of CO is carried out on $Cu/ZnO/Al_2O_3$ catalysts at 190–240 °C [1]. The performance of the WGS reaction stage, which much depends on quality of the catalysts, determines substantially the production cost of synthesis gases and hydrogen [2,3]. This quality is especially important in the case of $Cu/ZnO/Al_2O_3$ catalysts, which, due to their nature are susceptible to chemical poisoning and can be easily deactivated thermally [4,5]. An improvement of LT-WGS catalysts of the type $Cu/ZnO/Al_2O_3$ has been a subject of continuous and ongoing interest of many research groups. The results published recently by Shishido et al. show a beneficial effect of some alkali earth metals on the catalytic activity [6]. Similar conclusions can be drawn from the investigations of Nishida et al. showing that the catalyst activities can be enhanced by an addition of precious metals, especially platinum [7]. According to Kam et al. [8] there is a possibility of achieving higher activity and stability by doping copper catalysts with lanthanum. There are many other kinds of catalysts with high activity towards LT-WGS reaction [9,10].

One of the essential performance disadvantages of copper catalysts for LT-WGS is their activity towards methanol synthesis (3), which is the main side reaction [11].

$$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O, \quad \Delta H = -49.5\,kJ/mol \tag{3}$$

Despite the fact that methanol formed during WGS causes several technological problems [12], there is relatively few research data on improving the catalyst selectivity. The sparse literature reports show that it is potentially possible to improve the selectivity of $Cu/ZnO/Al_2O_3$ catalysts and to eliminate or at least reduce the formation of methanol by doping the conventional catalysts with alkali metals [13,14].

In order to verify these findings and to determine the quantitative influence of the addition of alkali metals, we have carried out physicochemical investigations and a kinetic evaluation of some samples of the same catalyst (analog of commercial catalysts) doped with different alkali metals (Li, Na, K, Cs) in equal amounts.

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1. Experimental

1.1. Sample preparation

A precursor of a standard $Cu/ZnO/Al_2O_3$ catalyst (molar composition $(Cu+Zn)/Al=4$ and $Cu/Zn=1.5$) was prepared by coprecipitation method. An aqueous solution of copper, zinc, aluminum nitrates (POCh Gliwice, Poland) and an alkali solution of sodium carbonate were added slowly to a beaker with 150 ml of redistilled water heated up to 65–70 °C. The reaction temperature was kept in the given range and the pH value of the resulting suspension was maintained in the range 7–7.4. Under these conditions the precursor deposited that was aged by means of intensive stirring within 1 h. In the next step the sodium and nitrate ions were thoroughly removed by washing out with redistilled water. Decantation of the material was followed by drying at 105 °C for 20 h.

The material obtained in this way was starting precursor for the preparation of alkali metals doped catalysts. They were prepared by incipient wetness impregnation method. The concentration of solutions (Cs_2CO_3 (Aldrich), $K_2CO_3{\cdot}1.5H_2O$, $Na_2CO_3{\cdot}10H_2O$, $LiNO_3{\cdot}3H_2O$ (POCh Gliwice)) used for impregnation was fixed on the basis of pore volume (0.6 ml/g) and desired level of promoter in the final catalyst. Four portions of the same standard precursor batch were weighed and placed separately into a rotating glass flask and impregnated one after another. The aqueous solution of the corresponding alkali metal salt was then added dropwise into the flask and mixed with the precursor material for 15 min. After this time the samples were dried at 105 °C for 16 h and calcined at 380 °C for 4 h.

1.2. Chemical composition

Chemical compositions of catalysts were determined by XRF method using a X'UNIQUE II-Philips spectrometer.

1.3. Powder X-ray diffraction (XRD)

X-ray diffraction was used to identify the structure of precursors and reduced form of the catalysts (obtained by passing the 5% H_2/Ar mixture and heating up at a rate of 5 °C/min–220 °C/4 h). The XRD measurements were performed with a HZG-diffractometer using Cu-K_α ($\lambda = 1.542$ Å) radiation with a manganese monochromator. A scintillate counter was used as a detector.

1.4. Reducibility

Temperature-programmed reduction (TPR) was used to determine the influence of alkali metals on temperature and intensity of reduction bands. A catalyst sample (30 mg) was placed into a U-shaped quartz tube under a flow of reduction mixture 6% H_2/Ar. The U-tube was placed in an electrically heated furnace and the temperature of the sample was gradually increased (5 °C/min) to 400 °C. The amount of hydrogen consumed was recorded as a function of time. The measurement conditions were optimized, and criterion number "k" was in the range $55 < k < 140$ [15]. The temperature, at which hydrogen reacts, and hydrogen consumption peak intensity are associated with a particular type of a copper oxides structure.

1.5. Copper surface area

Active copper surface area measurements were carried out using chemisorption of N_2O-impulse technique [16,17]. Nitrous oxide reacts with superficial metallic copper with evolution of nitrogen (4). The amount of nitrogen generated is proportional to the copper surface area.

Table 1
Chemical composition of $Cu/ZnO/Al_2O_3$ catalysts.

Nr	Symbol	Promoter	Alkali metal content (as oxides)	
			[μmol/g_{kat}]	[% wt]
1	CuZnAl4_15	–	<2 ppm	<2 ppm
2	CuZnAl4_15_Li	Li_2O	42.2	0.13
3	CuZnAl4_15_Na	Na_2O	42.5	0.26
4	CuZnAl4_15_K	K_2O	41.7	0.39
5	CuZnAl4_15_Cs	Cs_2O	41.3	1.20

$$2Cu + N_2O \rightarrow Cu{-}O{-}Cu + N_2 \qquad (4)$$

The following surface oxide stoichiometry and density of surface copper atoms were assumed: $Cu/O = 2$ and 1.46×10^{19} at/m^2, respectively.

1.6. Activity tests

Catalyst activity for WGS reaction measurements was carried out under conditions similar to performance parameters of industrial LT-WGS catalysts. A differential 4-channel Tiomkin-type reactor [18] was applied. Detailed description of its construction was presented elsewhere [19].

Activity measurements conditions:

- process gas volume [l/h]: 55;
- catalyst grain size [mm]: 0.1–0.2;
- pressure [MPa]: 2.5
- temperature [°C]: 200–240
- dry gas composition [% mol]: 2% CO, 10% CO_2, 66% H_2, 22% N_2
- H_2O/dry gas ratio [mol]: 2

Process gas saturated with water steam was introduced to the multichannel reactor. Chemical composition of products was determined using a PU 4500 gas chromatograph equipped with a carbon oxides methanator and an FID detector.

Evaluation of alkali metals influence on methanol formation on $Cu/ZnO/Al_2O_3$ was carried out by methanol synthesis rate measurements under conditions similar to LT-WGS process, at process gas composition corresponding to LT-WGS equilibrium ($CO_2 + H_2 + H_2O$). Methanol synthesis rate was determined on the basis of its content in process condensate using a GC UNICAM 610 gas chromatograph with an FID.

Methanol reaction rate under LT-WGS conditions:

- catalyst grain size [mm]: 0.1–0.2;
- temperature [°C]: 200–240;
- pressure [MPa]: 2.45;
- dry gas composition [% mol]: 20% CO_2/H_2;
- H_2O/dry gas ratio [mol]: 0.3

1.7. Thermostability tests

Thermal stability evaluation was based on comparison of copper surface area changes before and after superheating at 400 °C for 24 h in a stream of $CO/H_2/CO_2/H_2O/N_2$ process gas.

2. Results

The results of a chemical composition determination of catalysts under investigation are summarized in Table 1.

The data in Table 1 show that thorough washing out results in a reference catalyst, having a very low content of alkali metals. The other catalysts prepared on a basis of the reference catalyst are

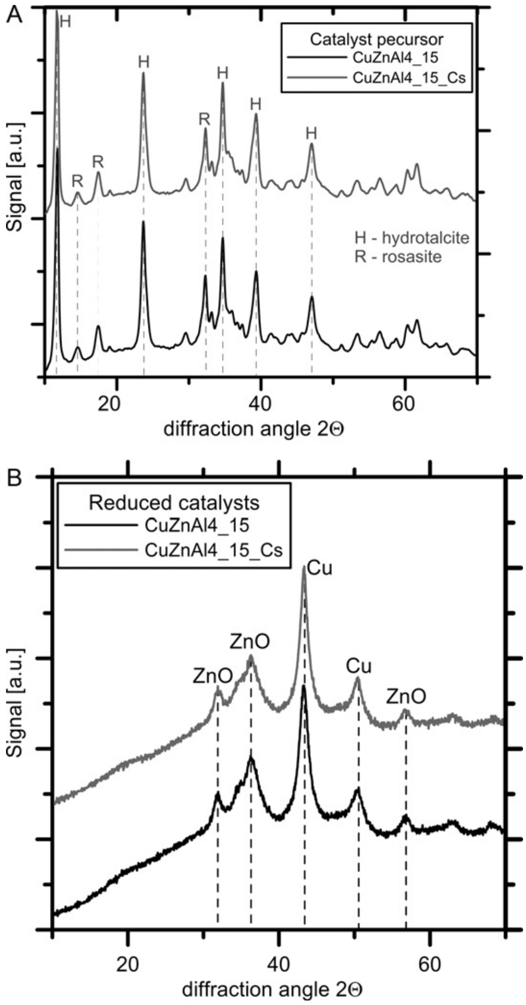

Fig. 1. The comparison of XRD patterns of standard and cesium doped samples (A – precursors, B – after reduction with 5%H_2/Ar).

characterized by almost identical content of alkali metal promoters (molarly).

The comparison analysis of XRD patterns of a standard precursor and the one doped with cesium enables to determine an influence of a cesium additive on the properties of the precursor material (Fig. 1). It seems reasonable to expand this influence on other alkali metals.

The intensity analysis of the corresponding diffraction bands reveals that, in the case of both reference precursor and the one with the cesium additive, hydrotalcite is a dominant crystal form. The presence of those phases is confirmed by intensive reflections in XRD patterns at diffraction angles $2\Theta = 11.8°$, 23.4°, 34.7°, 39.4° and 47.2°. Moreover, precursors contain also rosasite phase as indicated by the presence of reflections at diffraction angles 14.7°, 17.6°, 32.4°. The XRD patterns of both samples are essentially very similar, small differences of band intensities indicate better formation of hydrated phases of basic copper–zinc–aluminum carbonates in samples without alkali metals. A similar situation takes place by comparison of results for oxides reduced to an active form. The spectra are characterized by almost identical shape of curves, indicating comparable composition of crystal phases. There are dominant refections at the diffraction angle of 43.2°, which can be assigned to reduced copper metal. The results of XRD studies show that the presence of alkali metals does not cause any substantial crystallographic changes in both a precursor and an active catalyst form.

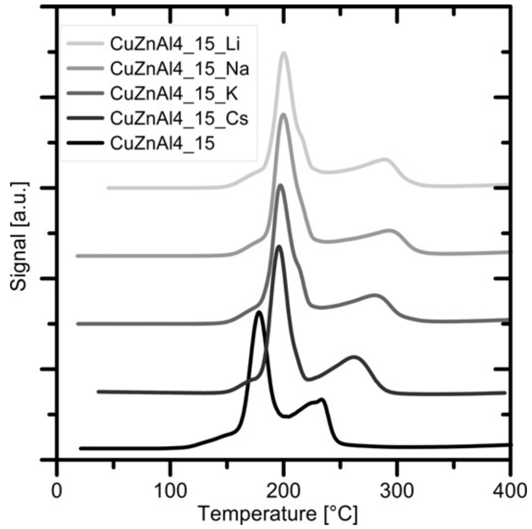

Fig. 2. TPR profiles of alkali metal doped catalysts.

The course of reduction processes is illustrated by TPR profiles in Fig. 2.

Reduction of all catalysts investigated proceeds in two steps. In the case of the reference catalyst there are two bands on TPR curve, a sharp reduction band in the range 170–200 °C and a broader one above 220 °C. A comparison with reduction profiles for other samples reveals that, independently of a type, an addition of an alkali metal results in a remarkable shift (by ca. 20–30 °C) of maximum reduction rate (for low temperature band) towards higher temperatures. The position of the second reduction band is also shifted towards higher temperatures by ca. 50–60 °C. A comparison of the TPR profile of the reference catalyst and doped forms leads to a conclusion that the addition of alkali metals makes the reduction of copper oxide forms more difficult, that the process runs at higher temperature, the intensities of reduction bands are lower (broadening of TPR profile).

A dependence between a surface area of copper and a type of alkali metal is shown in Fig. 3. These data show that the presence of alkali metals in a catalyst causes unfavorable decrease of copper active surface. The presence of alkali metals decreases this active

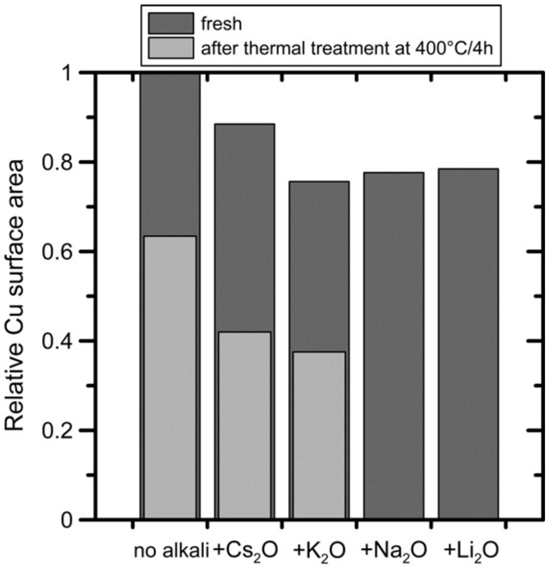

Fig. 3. The influence of alkali metal addition on copper surface area.

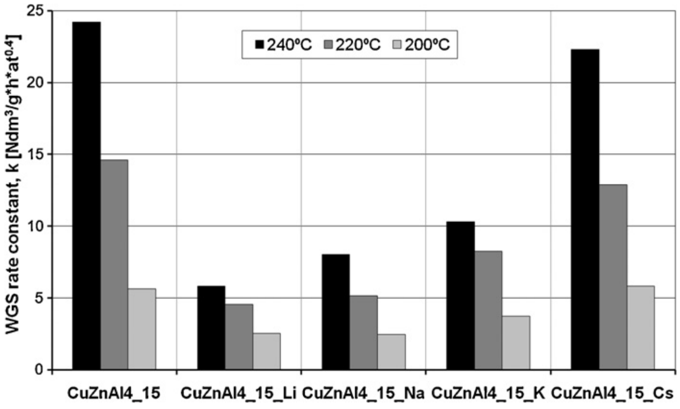

Fig. 4. The comparison of WGS rate constants for catalysts doped with alkali metals with 42 μmol/g_{kat}.

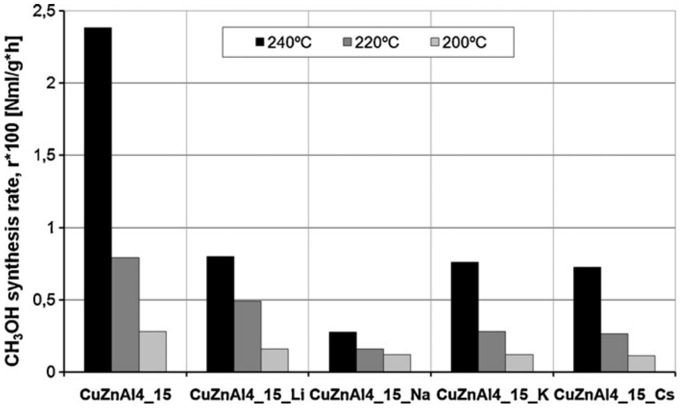

Fig. 5. The comparison of methanol synthesis rate for alkali metals doped catalysts.

surface by 10–20%, with the largest decrease being observed for potassium and the lowest for cesium.

The influence of the type of alkali metal promoters is more pronounced in the case of catalysts, which are a subject of thermal treatment at 400 °C, simulating the "aging" process. The alkali metals clearly favors recrystallization processes of copper. In both cases of the catalysts doped with potassium and cesium the copper surface decreases by ca. 60% with respect to the reference catalyst. The identical thermal treatment of the catalyst without any additives results in a decrease of copper surface by only 40%.

The results of activity in a kinetic regime under industrial process conditions (2.5 MPa) in WGS are summarized in Fig. 4.

The activity of catalysts containing alkali metal additives in WGS processes is remarkably lower than that of the reference catalyst. The consequences of incorporation of various additives can be different. Significant decrease of activation energies and preexponential factors have been observed. Their values correlate with each other, manifesting the compensation effect [20]. The disadvantageous effect of alkali metals on the activity in WGS decreases in the order: $Cs \ll K < Na < Li$. Only the cesium doped catalyst exhibited properties that are similar to those for the standard catalyst.

The results of activity in a kinetic regime under industrial conditions (2.5 MPa) towards methanol synthesis are summarized in Fig. 5 (Table 2).

A comparison study of catalytic activity shows a remarkable inhibiting influence of alkali metals on methanol synthesis (with the same concentration in catalyst). In comparison with the reference catalyst the activity of catalysts doped with alkali metals is at least four times lower (at 240 °C). This influence seems to be similar for Li, K, and Cs but greater in the case of Na.

3. Discussion

The addition of alkali metals to Cu–Zn–Al catalysts causes textural changes. The thermal treatment of precursors containing alkali metals leads to the catalysts with a decreased specific surface in comparison with reference systems. This decrease of surface is very distinct already by low concentrations of alkali metals in the system and can be rationalized by mechanical clogging of catalyst micropores or preferential localization of alkali promoter on Al_2O_3 (basic structure-forming factor).

Table 2
Kinetic parameters for a series of alkali doped catalysts.

	Symbol	Preexponential factor	Apparent activation energy [kJ/mol]
1	CuZnAl4_15	4.98×10^8	71.9
2	CuZnAl4_15_Li	1.74×10^5	43.7
3	CuZnAl4_15_Na	7.06×10^6	58.2
4	CuZnAl4_15_K	1.22×10^8	67.9
5	CuZnAl4_15_Cs	3.24×10^7	61.1

The results of investigations on reducibility of Cu–Zn–Al catalysts doped with alkali metals are quantitatively consistent with literature data. The presence of alkali metals hinders reduction of copper oxide forms. In the case of compounds investigated, namely Cs_2CO_3 and K_2CO_3, their inhibiting effect is probably due to the formation of quasi-passivated copper or copper carbonates [21] forms and stabilization of Cu^+ species. This finding is confirmed by the shape of TPR profiles, especially by decrease of intensity of reduction bands and their shift towards higher temperatures for catalysts containing Cs_2O and K_2O.

The addition of alkali metals to the $Cu/ZnO/Al_2O_3$ catalyst cause a decrease of copper surface, presumably because of partial blocking of copper atoms by superficial carbonates or by decreased copper dispersion. It seems that the surface area is to some extent influenced by recrystallization of catalyst components in the presence of alkali metals already in the calcination step (conducted at 380 °C). The results of chemisorption reveal that sintering of the active copper proceeds more intensive in the presence of alkali metal compounds on the catalyst surface. A comparison of results obtained with literature data on sodium compounds leads to the conclusion that similar effects are induced by all alkali metals compounds. This effect becomes more pronounced during overheating. Therefore, the addition of alkali metals, especially in larger concentrations can decrease the thermostability of the catalysts. The above mentioned results of our investigations show quite disadvantageous influence of alkali metals on physicochemical properties of LT-WGS catalysts.

Based on the results of kinetic measurements one can conclude that the addition of cesium and potassium compounds decreases the catalytic activity in WGS process and that cesium exerts no promoting influence on the activity in WGS. However, the kinetic results show a very positive effect of the alkali metals additives on remarkable inhibition of methanol synthesis, accompanying by a relatively small influence on the activity towards WGS.

4. Conclusions

The incorporation of alkali metals compounds onto Cu–Zn–Al catalysts significantly changes their physicochemical and kinetic properties.

1. Process of CuO reduction into active metallic copper runs at higher temperature range. Specific surface area and active copper surface area are lower for alkali doped catalysts comparing to alkali-free ones.

2. Recrystallization of active copper is more intensive for alkali doped than for standard Cu–Zn–Al catalysts. The presence of alkali metals on Cu–Zn–Al catalyst surface decreases its thermal stability.
3. Significant decrease of activity has been observed as an effect of alkali compounds addition, WGS activity decreases in the order: alkali-free $\approx$Cs $\ll$ K < Na < Li.
4. Cu–Zn–Al catalyst doping with alkali metal compounds results in radical inhibition of methanol synthesis at LT-WGS conditions process.

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